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(54) **Combating insect infestation in rice with diacyl hydrazines**

(57) A method for combating insect infestation in rice uses an insecticidally active N'–substituted–N, N'–diacylhydrazine of formula A–CO–NH–N(R)–CO–A' [wherein R is *tert*–butyl or neopentyl; A is a 2–pyridyl or phenyl, the phenyl ring being optionally substituted with one or two substituents independently selected from halo, methyl, ethyl, methoxy, or ethoxy; and A' is 1-methylethenyl or phenyl, the phenyl ring being optionally substituted with one or two substituents independently selected from halo, methyl or ethyl].

The invention also encompasses a vendible article which comprises a container, an insecticidally active N'–substituted–N, N'–diacylhydrazine and instructing information for applying said active compound to rice plants or seeds or to their growth medium or environment.

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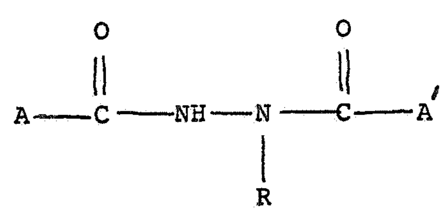
Combating Insect Infestation in Rice

The present invention concerns a vendible article and a method for combating insect infestation in rice.

More specifically, though not exclusively, the invention concerns a method for combating insect infestation in rice by applying an insecticidally active compound of the formula:



FORMULA 1

wherein R is <u>tert</u>-butyl or neopentyl; A is 2-pyridyl, phenyl or phenyl substituted with one or two substituents each independently selected from the group consisting of 2- or 4-halo, 2,3- or 2,6- dihalo, 4-(C_1-C_2)alkyl, 2,3-di(C_1-C_2)alkyl, 2-(C_1-C_2)alkyl-3-halo, 2-halo-3-(C_1-C_2)alkyl, 2,3-di(C_1-C_2)alkoxy and 2- or 3- (C_1-C_2)alkoxy; A' is 1-methylethenyl, phenyl or phenyl substituted with one or two substituents each independently selected from 2-, 3-, or 4-halo, 3,5- 3,4- or 2,4-dihalo, 3-(C_1-C_2)alkyl, 3,5-di(C_1-C_2)alkyl, 3-(C_1-C_2)alkyl-5-halo and 2-halo-5-(C_1-C_2)alkyl, provided A and A' are not both (unsubstituted) phenyl; or agronomically acceptable salts thereof ; to either growing rice plants, or rice seeds, or an area where or a medium in which rice plants are to be grown or are growing. The insecticidally active compound may be applied in a Composition which comprises, in addition to said active compound, an agronomically acceptable diluent or carrier. The composition may also contain another different Compound which is also effective at combating insect infestation in rice.

In Another aspect of the present invention, we provide a vendible article which comprises :

(1) a container,

(2) an insecticidally active compound of the formula:

$$A-\overset{O}{\overset{\|}{C}}-NH-\underset{R}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-A'$$

wherein R is <u>tert</u>-butyl or neopently;

A is 2-pyridyl, unsubstituted phenyl or phenyl substituted with one or two substituents each independently selected from the group consisting of 2- or 4-halo, 2,3- or 2,6-dihalo, 4-(C_1-C_2)alkyl, 2,3-di(C_1-C_2)alkyl, 2-(C_1-C_2)alkyl-3-halo, 2-halo-3-(C_1-C_2)alkyl, 2,3-di(C_1-C_2)alkoxy and 2- or 3-(C_1-C_2)alkoxy; A' is 1-methylethenyl, unsubstituted phenyl

or phenyl substituted with one or two substituents each independently selected from 2-, 3-, or 4-halo, 3,5-3,4- or 2,4-di halo, 3-(C_1-C_2)alkyl, 3,5-di(C_1-C_2)alkyl, 3-(C_1-C_2)alkyl-5-halo, 2-halo-5-(C_1-C_2)alkyl, provided A and A' are not both unsaturated phenyl; or an agronomically-acceptable salt thereof; contained within the container, and

(3) instructing information comprising written and/or illustrative information for applying the active compound to either growing rice plants, or rice seeds, or an area where or a medium in which rice plants are to be grown or are growing. The active compound may be in a composition which also comprises agronomically acceptable diluent or carrier. The composition may contain another different compound which is also effective at combating insect infestation in rice. The container is preferably a box, pail, drum or canister. Preferably, the instructing information is on an outside surface of the container, for example on the outside surface of the wall, lid or base of a box, pail or drum. The instructing information may be applied directly to the outside surface of the container or said information may be on a Label adhered to an outside surface of the container. Alternatively, the instructing information may be on an inside surface of the container; for example the information may be on the inner surface of the lid of a box, pail or drum; or on an inner surface of a wall of a cardboard box (in which case the active compound will probably have to be removed from the box, and the box possibly dismantled, for the instructions to be read); or the walls of the container may be transparant and the instructions read from the outside. In another embodiement, the instructing information is on a sheet of paper, or other suitable substrate, which may be either contained within the container; or detattachably, but not permanently, attached to an outer surface of the container e.g. the information may be on a sheet of paper held within an envelope which is adhered to the outside of the container, or simply held to the container by a rubber band.

The terms "Control" and "Combat" as employed in the specification and claims of this application are to be construed as including "insecticidal" and the protection of plants from insect damage. By "insecticidally effective amount" or "pesticidally effective amount" is meant that dosage of active substance sufficient to exert insect "Control" or to "Combat" insects.

The term halo as it applies to this invention means chloro, fluoro, bromo and iodo atoms.

The preferred moiety for the R substituent is tert-butyl. Preferred moieties for the A substituent are phenyl and substituted phenyl wherein the substituents are 4-halo, 4-(C_1-C_2)alkyl or 2,3-di(C_1-C_2)alkyl or 2,6-dihalo, preferably 2,6-difluoro. Preferred moieties for the A' substituent are substituted phenyls wherein the substituents are 2-halo, 2,4-dihalo, 3-(C_1-C_2)alkyl or 3,5-di(C_1-C_2)alkyl.

More preferred moieties for the A substituent are phenyls substituted with 4-methyl, 4-ethyl, 2,6-difluoro or 2,3-dimethyl and more preferred moieties for the A' substituent are phenyls substituted with 2-chloro, 2,4-dichloro, 2-chloro-4-fluoro, 3-methyl or 3,5-dimethyl.

More preferred compounds of Formula I for use in controlling insect pests of rice are: 1-(3,5-dimethylbenzoyl)-2-(4-ethylbenzoyl)-1-tert-butylhydrazine, 1-(3-methylbenzoyl)-2-(2,3-dimethylbenzoyl)-1-tert-butylhydrazine, 1-(3,5-dimethylbenzoyl)-2-(4-methylbenzoyl)-1-tert-

butylhydrazine, 1-(2-chloro-4-fluorobenzoyl)-2-benzoyl-1-tert-butylhydrazine and 1-(2,4-dichlorobenzoyl)-2-(2,6-difluorobenzoyl)-1-tert-butylhydrazine.

The compounds of Formula I exhibit several properties which make them particularly advantageous for use in rice crops and for use in pesticidal compositions used in rice. For example, the compounds exhibit high toxicity against many important insects which invade rice, including those of the orders Lepidoptera and Homoptera.

Another advantage of the compounds of Formula I is their low toxicity against mammals, birds, crustaceans and fish as well as beneficial insects such as lady beetles, which feed on aphids and scale pests, spiders, flys, wasps and true bugs of the order Hemiptera. This makes these compounds particularly suitable for use in rice since fish and crustaceans, e.g., shrimp, are often raised in rice paddies and geese and ducks are often used to control other insects in the vicinities of rice paddies. Moreover, rice paddy water usually flows or migrates into other water sources which are used by mammals, birds, crustaceans and fish.

The diacylhydrazines of Formula I are readily absorbed by the rice root system and exhibit systemic activity in the rice. This property makes the compounds particularly useful in controlling rice borers which are difficult to control by foliar dust or spray applications of insecticides. Moreover, the systemic distribution of the compounds in the rice plants may result in the need for fewer applications. Additionally, because the compounds cause little adverse effect on rice, the compounds are particularly useful in rice where phytotoxicity effects are considered highly undesirable.

The compounds used in the present invention are useful against rice Lepidoptera belonging to the families: (1) Pyralidae, rice borers, for example, spotted stalk borer (Chilo partellus Swinhoe), rice stem borer (Chilo suppressalis (Wlk.)), white rice borer (Maliarpha separatella Rag.), rice case worm (Nymphula depunctalis (Gn.)), rice leafroller (Cnaphalocrocis medinalis (Guen.)) and yellow and white paddy stem borers (Tryporyza incertulas (Wlk.) and T. innotata (Wlk.)); (2) Noctuidae, rice armyworms, for example, Mythimna unipuncta (Haw.) M., separata (Wlk.) and M. loreyi (Dup.), purple stem borer (Sesamia inferens (Wlk.)), beet armyworm (Spodoptera exigua (Hb.)) and paddy armyworm (Spodoptera mauritia (Boisd.)); and (3) Hesperidae, rice skippers, for example rice skippers (Telicota augias (L.)), Pelopidas mathias (F.)) rice leaf scaler (Parnara guttata (Bremer & Grey), and Ampittia dioscorides.

The compounds used in the present invention are also useful against rice Homoptera belonging to the families: (1) Cicadellidae, leaf-hoppers, for example, green leafhoppers (Nephotettix cinctinceps (Uhl.) and Nephotettix impicticeps Ishiwara), green rice leafhopper (Nephotettix nigropictus (Stal.)) and zig-zag winged leafhopper (Inazuma dorsalis (Motsch.)); and (2) Delphacidae, planthoppers, for example, brown planthopper (Nilaparvata lugens (Stal.).

The compounds used in the present invention are especially effective against larvae of Lepidoptera, particularly rice stem borer (Chilo suppressalis (Wlk.)), rice leaf folder or rice leaf roller (Cnaphalocrcis medinalis (Guen.)), rice armyworms (Spodoptera sp.)) and rice skipper (Telicota augias (L.)) and nymphs of Homptera, particularly green rice leafhopper (Nephotettix cincticeps (Uhl)).

When the compounds of Formula I have A as phenyl or a substituted phenyl, A' as 1-methylethenyl, phenyl or a substituted phenyl and R as tert-butyl or neopentyl, they can be prepared by Process A:

$$\underset{\text{II}}{\text{A-C(O)-Cl}} + \underset{\text{III}}{\text{NH}_2\text{NHR}} \xrightarrow[\text{Solvent}]{\text{Base}} \underset{\text{IV}}{\text{A-C(O)-NH-NHR}}$$

$$\underset{\text{IV}}{\text{A-C(O)-NH-NHR}} + \underset{\text{V}}{\text{A'-C(O)-Cl}} \xrightarrow[\text{Solvent}]{\text{Base}} \underset{\text{I}}{\text{A-C(O)-NH-NR-C(O)-A'}}$$

In process A, a compound of Formula II is reacted with an equivalent of a monosubstituted hydrazine of Formula III or a corresponding acid addition salt such as the hydrochloride salt or the like in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford an intermediate product of Formula IV which can be isolated or further reacted with a compound of Formula V in the presence of a base in an inert or substantially inert solvent or mixture of solvents to yield the desired product of Formula I.

When A and A' are the same, for example, both A and A' are 4-chlorophenyl, two equivalents of a compound of Formula II or V are reacted with an equivalent monosubstituted hydrazine of Formula III in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford the desired product of Formula I. The

compounds of Formula II and/or Formula V are generally commercially available or can be prepared by known procedures.

Compounds of Formula III which are used in the above process are t-butylhydrazine and neopentylhydrazine. These are commercially available and can be prepared by known procedures. For example, the Grignard reagent addition product of acetone azine in diethyl ether is hydrolyzed by the addition of an acid (such as oxalic acid), in a suitable solvent or mixture of solvents (such as ethanol and diethyl ether, 1:1) to produce the monosubstituted hydrazine of Formula III.

Suitable solvents for use in the above processes include water; alcohols such as methanol, ethanol, isopropanol and the like; hydrocarbons such as toluene, xylene, hexane, heptane and the like; glyme; tetrahydrofuran; acetonitrile; pyridine; or haloalkanes such as methylene chloride or mixtures of these solvents.

Preferred solvents are water, toluene, methylene chloride or a mixture of these solvents.

Examples of bases for use in the above process include tertiary amines such as triethylamine; pyridine; potassium carbonate; sodium carbonate; sodium bicarbonate; sodium hydroxide; or potassium hydroxide. Preferred bases are sodium hydroxide, potassium hydroxide or triethylamine.

Substantially equimolar amounts of reactants are preferably used, although higher or lower amounts can be used if desired.

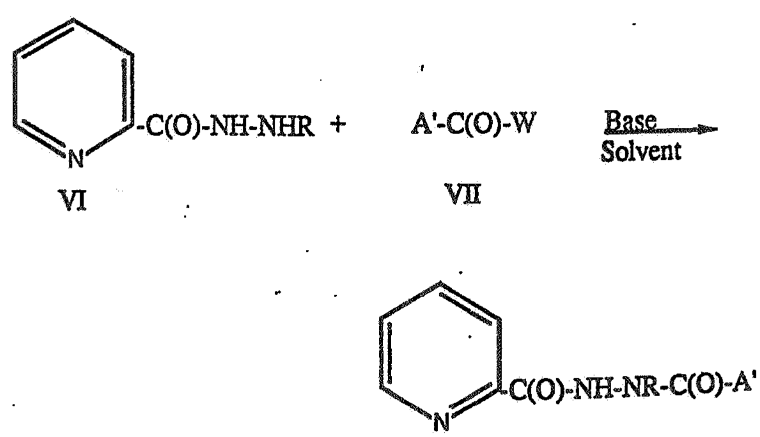
Generally, about one equivalent of base is used per equivalent of starting material of Formula II and V. Where the acid addition salt of the monosubstituted hydrazine of Formula III is used, one additional equivalent of base is used. For example, when substituents A and A'

are the same and a monosubstituted hydrazine is used, about two equivalents of base are used since about two equivalents of a suitably substituted benzoyl chloride of Formula II or V are employed. When substituents A and A' are different and an acid addition salt of the monosubstituted hydrazines of Formula III is used, about two equivalents of base are used in Step 1 and about one equivalent of base is used in Step 2.

Process A can be carried out at temperatures between about -20°C and about 100°C, preferably between about -5°C and about 50°C and preferably at about atmospheric pressure, although higher or lower pressures can be used, if desired.

When the compounds of Formula I have A as 2-pyridyl and A' and R as defined in Formula I, they can be prepared by Process B or Process C:

Process B



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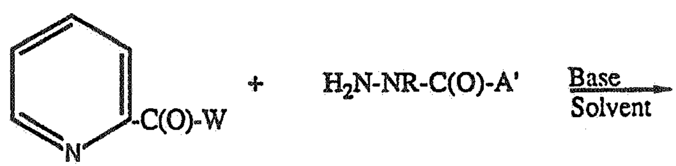
where W is a strong leaving group such as halo, for example, chloro; an alkoxy, for example, ethoxy; a methyl sulfonate (-OSO_2CH_3); or an ester, for example, acetate (-OC(O)CH_3).

In Process B, a compound of Formula VI is reacted with a compound of Formula VII in the presence of a base in an inert or substantially insert solvent or mixture of solvents to produce the desired product of Formula I.

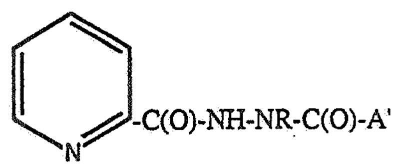
Examples of the compounds of Formula VII which can be used in the above Process B include benzoyl chloride, 2-bromobenzoyl chloride, 3,4-dichlorobenzoyl chloride, 2-iodobenzoyl chloride, 2,4-dichlorobenzoyl chloride, 4-fluorobenzoyl chloride, 2-chloro-5-methylbenzoyl chloride, 2-chloro-4-fluorobenzoyl chloride and the like. The compounds of Formula VII are generally commercially available or can be prepared by known procedures.

The compounds of Formula VI are prepared from commercially available compounds by procedures well known to those skilled in the art. By way of example, a suitably substituted hydrazine (such as t-butylhydrazine) is reacted with a pyridyl ester (such as ethyl 2-pyridylcarboxylate in an inert or substantially inert solvent or mixture of solvents (such as ethanol), with heat, to yield the compounds of Formula VI (such as 1-(2-pyridylcarbonyl)-2-t-butylhydrazine.

Process C



VIII IX



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where W is a good leaving group such as halo, for example, chloro; an alkoxy, for example, ethoxy; methyl sulfonate ($-OSO_2CH_3$); or an ester, for example, acetate ($-OC(O)CH_3$).

In Process C, an 1-substituted-1-benzoylhydrazine of Formula IX is reacted with a compound of Formula VIII in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford the desired product of Formula I.

The compounds of Formula VIII are generally commercially available or can be prepared from commercially available compounds by procedures well known to those skilled in the art as described below.

Examples of the compounds of Formula IX which can be used in the above Process C include 1-t-butyl-1-benzoylhydrazine; 1-t-butyl-1-(3-

methylbenzoyl)hydrazine; 1-t-butyl-1-(4-chlorobenzoyl)hydrazine; 1-t-butyl-1-(2-fluorobenzoyl)hydrazine; 1-neopentyl-1-(4-chlorobenzoyl)hydrazine, and the like.

Suitable solvents for use in Processes B and C include water; hydrocarbons such as toluene, xylene, hexane, heptane and the like; alcohols such as methanol, ethanol, isopropanol and the like; glyme; tetrahydrofuran; acetonitrile; pyridine; or haloalkanes such as methylene chloride; or mixtures of these solvents. Preferred solvents are water, toluene, methylene chloride or a mixture of these solvents.

Examples of bases suitable for use in Process B and C include tertiary amines such as triethylamine; pyridine; potassium carbonate; sodium carbonate; sodium bicarbonate; sodium hydroxide; or potassium hydroxide. Preferred bases are sodium hydroxide, or triethylamine.

The above Processes B and C can be carried out at temperatures between about -50°C and about 150°C. Preferably, when W is a halo radical, the reaction is carried out between about 0°C and about 30°C. When W is alkoxy, the reaction is preferably carried out between about 100°C and about 150°C. When W is methyl sulfonate, the reaction is preferably carried out between about -20°C to about 20°C. When W is an ester, the reaction is preferably carried out between about 0°C and about 50°C.

Preparation of the compounds using Processes B and C is preferably carried out at about atmospheric pressure, although higher or lower pressures can be used if desired.

Substantially equimolar amounts of reactants are preferably used in Processes Band C, although higher or lower amounts can be used if desired.

Generally, about one equivalent of base is used per equivalent of the reactant of Formula VI and VIII.

The agronomically acceptable salts embraced by Formula I of the invention can be prepared by reacting a metal hydroxide, a metal hydride or an amine or ammonium salt, such as a halide, hydroxide or alkoxide with a compound of Formula I having one or more hydroxy or carboxy groups or reacting a quaternary ammonium salt, such as chloride, bromide, nitrate or the like with a metal salt of a compound of Formula I in a suitable solvent. When metal hydroxides are used as reagents, useful solvents include water; ethers such as glyme and the like; dioxane; tetrahydrofuran; alcohols such as methanol, ethanol, isopropanol and the like. When metal hydrides are used as reagents, useful solvents include nonhydroxylic solvents, for example, ethers such as dioxane, glyme, diethylether and the like; tetrahydrofuran; hydrocarbons such as toluene, xylene, hexane, pentane, heptane, octane and the like; dimethylformamide, and the like. When amines are used as reagents, useful solvents include alcohols, such as methanol or ethanol; hydrocarbons, such as toluene, xylene, hexane and the like; tetrahydrofuran; glyme; dioxane; or water. When ammonium salts are used as reagents, useful solvents include water; alcohols, such as methanol or ethanol; glyme; tetrahydrofuran; or the like. When the ammonium salt is other than a hydroxide or alkoxide, an additional base, such as potassium or sodium hydroxide, hydride, or alkoxide is generally used. The particular choice of solvent will depend on the

relative solubilities of the starting materials and the resultant salts, and slurries rather than solutions of certain reagents may be used to obtain the salts. Generally, equivalent amounts of the starting reagents are used and the salt-forming reaction is carried out at about 0°C to about 100°C, preferably at about room temperature.

The acid addition salts of the present invention can be prepared by reacting hydrochloric, hydrobromic, sulfuric, nitric, phosphoric, acetic, propionic, benzoic or other suitable acid with a compound of Formula I having a basic functional group in a suitable solvent. Useful solvents include water, alcohols, ethers, esters, ketones, haloalkanes and the like. The particular choice of solvent will depend on the relative solubilities of the starting materials and the resulting salts and slurries rather than solutions of certain reagents may be used to obtain the salts. Generally, equivalent molar amounts of starting materials are used and the salt-forming reaction is carried out at from about -10°C to about 100°C, preferably at about room temperature.

The following examples will further illustrate this invention but are not intended to limit it in any way.

Example 4 - Preparation of 1-(3,5-dimethylbenzoyl)-2-(4-ethylbenzoyl)-1-tert-butylhydrazine.

To a stirred suspension of t-butylhydrazine hydrochloride (1.24 gm, 10 m moles) in toluene (30 ml) at room temperature was added dropwise a 50% aqueous solution of sodium hydroxide (0.8 gm, 10 m mole). After 15 min., the reaction mixture was cooled to 5°C and a solution of 4-ethylbenzoyl chloride (1.69 gm, 10 m mole) in toluene (5 ml) and a solution of aqueous 50% sodium hydroxide (0.8 gm, 10 m

mole) were added dropwise simultaneously from separate addition funnels while maintaining the temperature at or below 10°C. Following the addition, the reaction mixture was warmed to room temperature and stirred for 1 hour. The reaction mixture was diluted with toluene and washed with water. The organic layer was separated, dried over anhydrous magnesium sulfate, and the solvent removed under vacuum to afford a yellow oil which slowly solidified on standing. The product was recrystallized from ether and hexane to yield white crystals.

To a stirred solution of the monobenzoylated compound (2.19 gm., 10 m moles) in toluene (30 ml) at 5°C, were added dropwise simultaneously from separate addition funnels, solutions of 3,5-dimethylbenzoyl chloride (1.69 gm., 10 m moles) in toluene (5 ml) and aqueous 50% sodium hydroxide solution (0.8 g) while maintaining the temperature below 10°C. Following the addition, the reaction mixture was warmed to room temperature and stirred for 1 hour. The mixture was then diluted with hexane and the precipitated product isolated by filtration. The product was washed with water and hexane and dried. The crude product was recrystallized from ether-methanol yielding 1-(3,5-dimethylbenzoyl)-2-(4-ethylbenzoyl)-1-tert-butylhydrazine: m.p. 181°C.

Example 15 - Preparation of 1-t-butyl-1(4-chlorobenzoyl)-2-benzoylhydrazine

To a stirred suspension of t-butylhydrazine hydrochloride (1.24 gm, 10 m moles) in toluene (30 ml) at room temperature was added dropwise a 50% aqueous solution of sodium hydroxide (0.8 gm, 10 m

mole). After 15 minutes, the reaction mixture was cooled to 5°C and a solution of benzoyl chloride (1.42 gm, 10 m mole) in toluene (5 ml) and a solution of aqueous 50% sodium hydroxide (0.8 gm, 10 m mole) were added dropwise simultaneously from separate addition funnels while maintaining the temperature at or below 10°. Following the addition, the reaction mixture was warmed to room temperature and stirred for 1 hour. The reaction mixture was diluted with toluene and washed with water. The organic layer was separated, dried over anhydrous magnesium sulfate, and the solvent removed under vacuum to afford a yellow oil which slowly solidified on standing. The product was recrystallized from ether and hexane to afford white crystals.

To a stirred solution of the monobenzoylated compound (1.92 gm., 10 m moles) in toluene (30 ml) at 5°C, were added dropwise simultaneously from separate addition funnels, solutions of 4-chlorobenzoyl chloride (1.75 gm., 10 m moles) in toluene (5 ml) and aqueous 50% sodium hydroxide solution (0.8 g) while maintaining the temperature below 10°C. Following the addition, the reaction mixture was warmed to room temperature and stirred for 1 hour. The mixture was then diluted with hexane and the precipitated product isolated by filtration. The product was washed with water and hexane and dried. The crude product was recrystallized from ether-methanol yielding 1-t-butyl-1-(4-chlorobenzoyl)-2-benzoylhydrazine as a white powder: m.p. 201-204°C.

Using the same procedure as used in this example, Examples 1-3, 6-14, 16-25 and 35-257 described in Tables 1 and 2 below were also prepared except the benzoyl chloride (Formula II of Process A) was: 2-bromo-3-methylbenzoyl chloride, 2-methyl-3-bromobenzoyl

chloride, 2-methyl-3-chlorobenzoyl chloride, 2-methyl-3-fluorobenzoyl chloride, 2,3-dimethylbenzoyl chloride, 3,5-dimethylbenzoyl chloride, 2-chloro-3-methylbenzoyl chloride, 2-chloro-6-fluorobenzoyl chloride, 2-chloro-3-methoxybenzoyl chloride, 2,3-dichlorobenzoyl chloride, 2,6-dichlorobenzoyl chloride, 2-ethyl-3-chlorobenzoyl chloride, 2-fluoro-3-methylbenzoyl chloride, 2-fluoro-3-chlorobenzoyl chloride, 2,3-difluorobenzoyl chloride, 2,6-difluorobenzoyl chloride, 3-methoxy-4-methylbenzoyl chloride, 2,3-dimethoxybenzoyl chloride, 2,5-dimethoxybenzoyl chloride, 3,4-dimethoxybenzoyl chloride, 2-bromobenzoyl chloride, 4-bromobenzoyl chloride, 4-methylbenzoyl chloride, 2-chlorobenzoyl chloride, 4-chlorobenzoyl chloride, 2-fluorobenzoyl chloride, 4-fluorobenzoyl chloride, 4-iodobenzoyl chloride, 2-methoxybenzoyl chloride, 3-methoxybenzoyl chloride, 4-ethylbenzoyl chloride, or benzoyl chloride,

and the 4-chlorobenzoyl chloride (Formula V of Process A) was:

2-bromo-4-chlorobenzoyl chloride, 2-bromo-4-fluorobenzoyl chloride, 2,4-dibromobenzoyl chloride, 3,5-dibromobenzoyl chloride, 3,5-dimethylbenzoyl chloride, 3-methyl-5-chlorobenzoyl chloride, 2-chloro-4-bromobenzoyl chloride, 2-chloro-5-methylbenzoyl chloride, 2-chloro-4-fluorobenzoyl chloride, 3-chloro-4-fluorobenzoyl chloride, 2-iodo-4-chlorobenzoyl chloride, 3-iodo-4-chlorobenzoyl chloride, 2,4-dichlorobenzoyl chloride, 3,4-dichlorobenzoyl chloride, 3,5-dichlorobenzoyl chloride, 2-fluoro-4-chlorobenzoyl chloride, 2,4-difluorobenzoyl chloride, 3,4-difluorobenzoyl chloride, 3,5-difluorobenzoyl chloride, 2-bromobenzoyl chloride,

3-bromobenzoyl chloride, 4-bromobenzoyl chloride, 3-methylbenzoyl chloride, 4-methylbenzoyl chloride, 2-chlorobenzoyl chloride, 3-chlorobenzoyl chloride, 4-chlorobenzoyl chloride, 3-ethylbenzoyl chloride, 2-fluorobenzoyl chloride, 3-fluorobenzoyl chloride, 4-fluorobenzoyl chloride, 2-iodobenzoyl chloride, 3-iodobenzoyl chloride, 4-iodobenzoyl chloride, benzoyl chloride, or vinylacetyl chloride.

Example 27 - Preparation of 1-t-butyl-1-benzoyl-2-(2-pyridinecarbonyl)hydrazine.

To a suspension of t-butylhydrazine hydrochloride (9.9gm, 0.794 mol) in absolute ethanol (50 ml) was added 50% aqueous sodium hydroxide (6. 35 gm). The mixture was stirred and warmed up while ethyl picolinate (12.0 gm) was added dropwise. The resulting mixture was allowed to reflux for about 3 days. After cooling, water was added and the product extracted with methylene chloride. The organic layers were washed with water and dried over magnesium sulfate. Evaporation of solvents afforded 1-t-butyl-2-(2-pyridinecarbonyl)-hydrazine as yellow oil which solidified on cooling.

A solution of the 1-t-butyl-2-(2-pyridinecarbonyl)hydrazine (1.0 gm. 0.00518 mol.) in 20 ml of toluene at 23°C was treated sequentially with 50% sodium hydroxide (1.3 gm) and benzoyl chloride (0.728 gm.) The mixture was stirred overnight. The solids were removed by filtration and washed with water to yield 1-t-butyl-2-(2-pyridinecarbonyl)-1-benzoylhydrazine: m.p. > 200°C.

Examples 26 and 28-34 were prepared in the same manner except instead of using benzoyl chloride, 4-fluorobenzoyl chloride (ex. 26), 2-

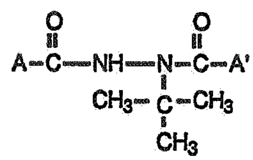
bromobenzoyl chloride (ex. 28), 3,4-dichlorobenzoyl chloride (ex. 30), 2-iodobenzoyl chloride (ex. 31), 2,4-dichlorobenzoyl chloride (ex. 32), 2-chloro-5-methylbenzoyl chloride (ex. 33) and 2-chloro-4-fluorobenzoyl chloride (ex. 34) were used.

Example 37 - Preparation of 1-t-butyl-1,2-bis(4-chlorobenzoyl)hydrazine

A suspension of t-butylhydrazine hydrochloride (12.5gm, 0.1 mole) in toluene (100 ml.) at 0-5°C was treated slowly with 1 equivalent of sodium hydroxide solution, prepared from diluting 8 gm of 50% Sodium hydroxide commercially available solution to 20 ml with water. At 0 to 5°C with mechanical stirring, 2 equivalents of 4-chlorobenzoyl chloride (35.9 gm, 0.2 mole) and 2 equivalents of Sodium hydroxide (16 gm of 50% sodium hydroxide diluted with water to 40 ml) were added dropwise separately and simultaneously from dropping funnels. The exothermic reaction was cooled down by an ice-water bath through the entire addition. After the addition was completed, the resulting suspension was stirred at room temperature for one hour. The white precipitate was collected by suction-filtration and washed with a small amount of toluene and 100 ml of water. The material was air-dried, then crystallized from 95% aqueous methanol to afford 24.65 gm of 1-t-butyl-1,2-bis(4-chlorobenzoyl)hydrazine as needles: m.p. 246-248°C.

Additional product can be obtained by concentrating the mother liquor of crystallization.

<u>TABLE 1</u>

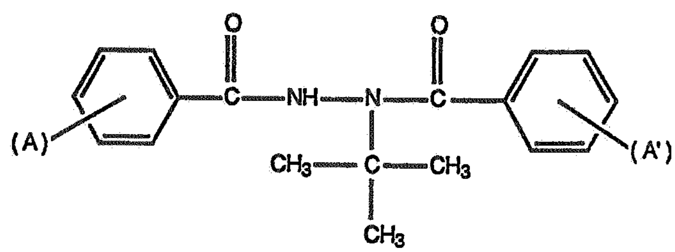


Example	A	A'
1	4-MeØ	3-MeØ
2	4-MeØ	3,5-Me_2Ø
3	4-MeØ	Ø
4	4-EtØ	3,5-Me_2Ø
5	2,3-Me_2Ø	2-BrØ
6	2,3-Me_2Ø	2,4-Cl_2Ø
7	2,3-Me_2Ø	3,5-Me_2Ø
8	2,3-Me_2Ø	3-MeØ
9	2Me,3ClØ	Ø
10	2Me,3ClØ	2Cl,4FØ
11	2Cl,3MeOØ	3,5-Me_2Ø
12	4EtØ	$CH_2C(=CH_2)CH_3$
13	Ø	2ClØ
14	Ø	3,4Cl_2Ø
15	Ø	4ClØ
16	Ø	3FØ
17	Ø	4FØ
18	Ø	2Br,4FØ
19	Ø	2BrØ

Example	A*	A'*
20	4FØ	4FØ
21	2FØ	2FØ
22	4ClØ	3ClØ
23	$2,6F_2Ø$	$2,4Cl_2Ø$
24	$2,6F_2Ø$	$3,5F_2Ø$
25	Ø	$CH_2C(=CH_2)CH_3$
26	2-pyridyl	4FØ
27	2-pyridyl	Ø
28	2-pyridyl	2BrØ
29	Ø	2Cl,4FØ
30	2-pyridyl	$3,4Cl_2Ø$
31	2-pyridyl	2IØ
32	2-pyridyl	$2,4Cl_2Ø$
33	2-pyridyl	2Cl,5MeØ
34	2-pyridyl	2Cl,4FØ
35	$2,3Me_2Ø$	$CH_2C(=CH_2)CH_3$

* Ø is phenyl.
Me is methyl.
Et is ethyl.
MeO is methoxy.

TABLE 2



Example	A	A'
36	H	3I,4Cl
37	4Cl	4Cl
38	2Cl	2Cl
39	4Me	4Cl
40	H	3Cl
41	H	3Me
42	H	2F
43	H	$2,4Cl_2$
44	4Cl	H
45	H	$3,5Cl_2$
46	2Cl	H
47	4Cl	$3,4Cl_2$
48	2Cl	$3,4Cl_2$
49	4Me	$3,4Cl_2$
50	4Me	$2,4Cl_2$
51	4Me	$3,5Cl_2$
52	4Me	2Cl

Example	A	A'
53	4Me	4F
54	4Cl	3Me
55	H	4Br
56	H	3Br
57	4Et	H
58	H	2Cl,4Br
59	H	2,4Br_2
60	H	3,5Me
61	4Cl	2Cl
62	4Cl	3,5Cl_2
63	4Cl	2,4Cl_2
64	4Me	3Cl
65	H	2I
66	H	3I
67	4Et	3Me
68	4Et	4Cl
69	2Br	H
70	3,4$(MeO)_2$	H
71	H	3Et
72	4Et	3Br
73	4Et	2I
74	2Br	2Br
75	4Et	3Et
76	4Me	3Br
77	H	4I
78	4Me	3Et

Example	A	A'
79	4Et	2,4Cl_2
80	2Cl	3Me
81	2Cl	2Br
82	2F	4Cl
83	2Cl	2,4Cl_2
84	2Cl	3Cl
85	2,6Cl_2	H
86	2Cl	4F
87	2Cl	4Br
88	2Cl	4Cl
89	2Cl	2F
90	3MeO	3Me
91	3MeO	H
92	3MeO	4Cl
93	3MeO	3,4Cl_2
94	2MeO	H
95	2MeO	3Me
96	2MeO	3,4Cl_2
97	2MeO	4Cl
98	2,6F_2	3,4Cl_2
99	2,6F_2	3Me
100	4Cl	3,5Me_2
101	3MeO	3,5Me_2
102	4Cl	2Br
103	4Cl	4F

Example	A	A'
104	4Et	2Br
105	$2,6F_2$	2Cl
106	$2,6F_2$	3Cl
107	$2,6F_2$	4Cl
108	$2,6F_2$	$3,5Me_2$
109	4F	H
110	4Et	$3,5Cl_2$
111	4Cl	2F
112	4Et	$3,4Cl_2$
113	4Et	2F
114	4Br	4Br
115	$2,6F_2$	$3,5Cl_2$
116	2F	2Br
117	2F	3Me
118	2F	H
119	2Me,3Cl	3Me
120	4Br	H
121	$2,3Cl_2$	2Br
122	$2,3Cl_2$	H
123	2F	3,5Me
124	$2,3Cl_2$	3Me
125	H	3Cl,4F
126	4Cl	3Cl,4F
127	$2,3Me_2$	$3,4Cl_2$
128	$2,3Me_2$	3Cl

Example	A	A'
129	$2,6F_2$	2Br
130	2Me,3Cl	$3,5Me_2$
131	2,Me,3Cl	3Cl,4F
132	$2,3Me_2$	3Cl,4F
133	4Et	3Cl,4F
134	2Cl,6F	3Me
135	$2,3(MeO)_2$	H
136	$2,3(MeO)_2$	4Cl
137	$2,3(MeO)_2$	2Br
138	2Me,3F	H
139	2Me,3F	3Me
140	2Cl,6F	H
141	2Cl,6F	4F
142	2Cl,6F	$2,4Cl_2$
143	$2,3F_2$	H
144	$2,3Cl_2$	$3,5Me_2$
145	$2,3Cl_2$	$2,4Cl_2$
146	$2,3Cl_2$	$3,5Cl_2$
147	$2,3Cl_2$	3Cl
148	$2,3F_2$	2Br
149	$2,3Me_2$	4Cl
150	$2,3Me_2$	$2,4F_2$
151	2Me,3Cl	$2,4Cl_2$
152	4Et	$3,5F_2$
153	$2,3Me_2$	2I

Example	A	A'
154	$2,3F_2$	3Me
155	$2,3F_2$	$3,5Me_2$
156	$2,3F_2$	$2,4Cl_2$
157	$2,3Me_2$	H
158	2Cl,3Me	$2,4Cl_2$
159	2Cl,3Me	H
160	2Cl,3Me	3Me
161	2Cl,3Me	$3,5Me_2$
162	2Cl,3Me	$3,5Cl_2$
163	$2,3Me_2$	2Cl
164	$2,3Me_2$	$3,5Cl_2$
165	$2,6F_2$	3Cl,4F
166	H	$3,4F_2$
167	4Cl	$3,5F_2$
168	$2,3Me_2$	$3,5F_2$
169	2Me,3Cl	$3,5F_2$
170	H	$3,5F_2$
171	2Me,3Cl	$3,5Cl_2$
172	2Br	$3,5Me_2$
173	2Cl,3Me	3Cl
174	$2,6F_2$	H
175	2Me,3Cl	3Cl
176	2Me,3Cl	4F
177	2Me,3Cl	2Br
178	2Cl,3MeO	3Me

Example	A	A'
179	2Cl,3MeO	H
180	2Cl,3MeO	2,4Cl_2
181	3MeO,4Me	3Me
182	2Me,3Br	H
183	2Me,3Br	3Me
184	2Me,3Br	4Cl
185	2Me,3Br	2,4Cl_2
186	3MeO,4Me	2Br
187	3MeO,4Me	2,4Cl_2
188	2Et,3Cl	H
189	2Et,3Cl	2,4Cl_2
190	2Br	3Me
191	2Br	2,4Cl_2
192	2F,3Me	H
193	2F,3Me	3Me
194	2F,3Me	3,4Cl_2
195	2F,3Me	2,4Cl_2
196	2F,3Me	4F
197	2F,3Me	3Cl
198	2,3Me_2	3Et
199	2F,3Me	3,5Me_2
200	2Br	3Cl
201	2Br	3,5Cl_2
202	2Br,3Me	3,5Me_2
203	2Br,3Me	2,4Cl_2

Example	A	A'
204	2Br,3Me	3Me
205	2Br,3Me	3,5Cl_2
206	2Br,3Me	2Br
207	2Br,3Me	3Cl
208	2Br,3Me	H
209	2Br,3Me	4F
210	2Br,3Me	2,4F_2
211	H	2,4F_2
212	2,6F_2	2,4F2
213	2,6F_2	2Cl,4F
214	2,3Me_2	2Cl,4F
215	2Cl,3MeO	2Br
216	2,3Me_2	2Br,4F
217	2F,3Cl	H
218	2F,3Cl	3,5Me_2
219	2F,3Cl	2,4Cl_2
220	2,3Me_2	3,5Br_2
221	4Et	3,5Br_2
222	H	3,5Br_2
223	3MeO	2Br
224	3MeO	2,4Cl_2
225	4I	H
226	4I	2,4Cl_2
227	4I	3,5Me_2
228	4Br	3Br

Example	A	A'
229	4Br	3,4Cl_2
230	4Et	3Cl
231	4Br	3,5Me_2
232	4Br	3Me
233	2,3Cl_2	3Cl,4F
234	2Me,3Cl	2,4F_2
235	2Me,3Cl	2Cl
236	2Me,3Cl	2Br,4F
237	2Me,3Cl	2F,4Cl
238	2,3Me_2	4F
239	2Cl	3,5Me_2
240	2F	4F
241	2F	2,4F_2
242	2F	2Cl,4F
243	2F	2,4Cl_2
244	H	2F,4Cl
245	2Cl	2Cl,4F
246	4Cl	2Cl,4F
247	4Et	2Cl,4F
248	4F	4Cl
249	2,6F_2	4F
250	2,3Me_2	3Br
251	2Cl	2,4F_2
252	2Cl	3F
253	2,5$(MeO)_2$	3,5Me_2

Example	A	A'
254	2,3Me_2	3Me,5Cl
255	4Cl	3Me,5Cl
256	H	2I,4Cl
257	H	2Br,4Cl

Insecticidal Examples

The compounds of Formula I were tested for their insecticidal activity using the following procedures.

a) Rice Stem Borer - Chilo suppressalis Wlk.) - foliar application.

Rice seedlings (var. Nippon-bare) at the budding stage were dipped in a 38 parts per million (ppm) test solution of each compound. (The test solution was prepared by dissolving the compound in a solvent of acetone and methanol (1:1 ratio), adding water to give a acetone: methanol: water system of 5:5:90 and then a surfactant was added. A 1:1 mixture of an alkylarylpolyetheralcohol (sold under the registered trademark Triton® X-155) and a modified phthalic glycerol alkyl resin (sold under the registered trademark Triton® B-1956) was utilized at the equivalent of 1 ounce per 100 gal. in the test solution as a surfactant. Unless usage of a formulated product has been specified, test solutions of compounds were prepared in like manner although the concentrations may differ among the insect species tested.) When the plants were dry, each seedling was placed in a Petri dish and infested with ten second instar larvae of the rice stem borer. The dish was covered and held for six days after which time the percent mortality, based upon dead and moribund larvae, was determined. The average

percent mortality over three such replicates per compound is shown in Table 3.

b) Ricehoppers - foliar application.

Brown Rice Planthopper - Nilaparvata lugens (Stal.)

Green Rice Leafhopper - Nephotettix cincticeps (Uhl.)

Rice seedlings (var. Nippon-bare) at the 4-leaf stage and maintained in glass beakers were sprayed with a 600 ppm test solution of each compound. When the spray had dried, each beaker was infested with a minimum of 100 second instar nymphs of either the green rice leafhopper or the brown planthopper (BRPH) and covered with a cloth. Eight days after infestation the number of insects alive was determined. The percent mortality was calculated on the basis of an initial population of 100 organisms. The average percent mortality over two such replicates per compound is shown for each test species in Table 3.

TABLE 3

Example	Percent Mortality Rice Stem Borer (38 ppm)	Brown Rice Planthopper (600 ppm)	Green Rice Leafhopper (600 ppm)
1	87	0	15
2	100	5	40
3	80	5	45
4	100	0	65
5	100	0	25
6	93	5	15
7	100	0	15
8	80	0	75
9	87	10	30
10	87	10	88
11	80	0	50
12	-	-	-*
13	100	5	98
14	73	0	15
15	80	10	25
16	73	0	60
17	87	0	55
18	93	10	25
19	87	0	80
20	93	5	15
21	100	0	45

* - Not Tested.

	Percent Mortality		
Example	Rice Stem Borer (38 ppm)	Brown Rice Planthopper (600 ppm)	Green Rice Leaf-hopper (600 ppm)
22	54	0	15
23	93	0	10
24	100	0	15
25	33	0	92
26	80	38	40
27	100	0	65
28	93	75	60

c) Rice Leaffolder or Rice Leafroller - Cnapthalocrocis medinalis (Guen.)

Five rice leaf blades (variety Kinmaze) were soaked for 30 seconds in a test solution containing 100 ppm of active ingredient of the compound of example 4, prepared from 10% aqueous flowable preparation of the compound. When dry, the rice blades were cut and placed on moist filter paper in a Petri dish and infested with five third instar rice leafroller larvae. The percent control was determined 6 days after infestation and the compound gave 100% control, i.e., all larvae had died.

d) Rice Stem Borer - Chilo suppressalis (Wlk.) - Systemic activity.

Rice plants (variety Nippon-bare) in the 7-8 leaf stage were grown in 1/5000 are Wagner pots. Compound of example 4 formulated as 239.7 grams per liter aqueous flowable (2F) preparation was

introduced onto the 3 cm deep water surface in these pots to provide a concentration equivalent to 1200 gm (a.i.)/ha (hectare). Eight days after treatment each pot was infested with 30 first instar rice stem borer larvae. Ten days after infestation, the plants were examined for the presence of live larvae. The percent control averaged over two replicates is shown and reflects correction for natural mortality as per Abbott's formula[1]. The compound of example 4 resulted in 97 percent mortality (corrected).

e) Southern Armyworm - Spodoptera eridania (Cramer) - foliar application.

Leaves were placed on moistened pieces of filter paper in Petri dishes. The leaves were then sprayed with a 600 ppm solution of a test compound using a rotating turntable and allowed to dry. The dishes were then infested with 10 third instar larvae of Southern armyworm and the dishes were covered. The percent mortality for the armyworm evaluations were determined 96 hours after treatment. Evaluations are based on a scale of 0-100 percent in which 0 equals no activity and 100 equals total kill.

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[1] Abbott, W.S., A Method of Computing the Effectiveness of an Insecticide. J. Econ. Entomol. 18 (2): 265-267 (1925).

i.e. $\frac{X - Y}{X} \times 100 = \%$ corrected mortality

where X = average % alive in the untreated check replicates and

Y = average % alive in the treated replicates.

Compounds of examples 1-33, 35-69, 71-76, 78-93, 95, 97-252 and 254-257 all gave 100 percent control; the percent control of examples 34 and 70 were 10; examples 77 and 94 were 90; and examples 96 and 253 were 30.

This activity against Southern armyworm, a Lepidoptera, is considered indicative of activity against rice Lepidoptera in view of the data presented in Table 3.

Toxicology Examples

A portion of the compounds used in this invention were tested to determine their toxicity against several different species of animals. The procedures and their results are given below. All these results are indicative of low toxicity.

a) Ames Test

Several of the compounds used in the present invention were tested in the Ames Test, a microbial mutagenicity assay. The compounds were tested against Salmonella typhimurium strains TA 1535, TA 1537, TA 98 and TA 100 according to the procedure described by Ames, et al., "Methods for Detecting Carcinogens and Mutagens with the Salmonella/Mammaliam-Microsome Mutagenicity Test", Mutation Research, 31: 347 (1975). The microsomal extracts were S-9 liver extract fractions from Aroclor 1254-induced rats. The microsomal extracts were tested with a positive control, which was a compound whose mutagenic activity required metabolic activation prior to use. The purpose of the positive control which was run with each assay, was to ensure that both the organism and the S-9 liver extract were

functional. The maximum concentration of the test compounds was 5,000 micrograms of active ingredient per plate. Examples 1, 2, 4, 6-9, 14, 15, 17 and 19 were tested and all tested negative, i.e., demonstrated no mutagenic activity.

b) Rats, Oral Toxicity

The acute oral toxicity of example 4 was assessed in male Crl:CD BR rats. The solid test substance was dispersed in corn oil and administered as a single oral dose by gavage (20 ml/kg) to a group of 10 male rats at a dosage of 5.0 gm/kg. A control group of rats received corn oil in the same manner. The rats were observed for 14 days. The rat oral LD_{50} (lethal dose required to kill fifty percent of the rats) for both examples 1 and 4 is greater than 5000 mg of compound per kilogram of body weight.

Examples 2, 6-9, 14, 15, 17 and 19 were run in the same manner except a single dose of 10 ml/kg was administered, a dosage of 500 mg/kg was used and there were 6 male rats per group. All of these compounds have rate oral LD_{50} values of greater than 500 mg/kg.

c) Rats, Dermal Toxicity

The acute dermal toxicity of Example 4 was assessed in male Crl:CD BR rats. The test substance, moistened with 0.85% saline (1:3 w/v), was applied to the clipped intact skin of six male rats at a dose of 5.0 gm/kg body weight. The application sites were covered with impervious cuffs for a period of 24 hours, after which the cuffs were removed and the sites wiped with water-soaked paper towels. A control group of six male rats were wrapped with cuffs in the same

manner but received no test substance. The rats were observed for 14 days. The rat acute dermal LD_{50} for example 4 was greater than 5,000 mg/kg.

Examples 1, 2, 6-9, 14, 15, 17 and 19 were tested in the same manner except the dose of these compounds were 200 mg/kg. All had LD_{50} values of greater than 200 mg/kg.

d) <u>Bobwhite Quail</u>

Example 4 was tested to determine the lethal dietary concentrations needed to kill 50% (LC_{50}) of Bobwhite quails. The compound was administered in the diet to groups (10 per group) of young quail (13-14 days old) at concentrations of 312, 625, 1,250, 2,500 and 5,000 ppm active ingredient for five days followed by three days of feeding on a control diet (recovery phase). The control population consisted of five separate groups of ten quails each. Observations for mortality , moribundity, and signs of intoxication were made daily. No mortalities were recorded in the test groups for the compound of example 4 or control groups throughout the study. The 8 day dietary LC_{50} of example 4 was determined to be greater than 5,000 ppm active ingredient.

e) <u>Mallard Ducks</u>

The compound of example 4 was tested to determine its LC_{50} in a ten-day dietary study of Mallard ducks. The test was run using the same procedure as for the Bobwhite quail except the ducklings were 7-8 days old. Two ducks from the group fed 5,000 ppm of example 4 died.

The 10 day dietary LC_{50} of example 4 was greater than 5,000 ppm active ingredient.

f) Daphnia magna

The susceptibility of Daphnia magna, a water flea, to example 4 was measured in 48 hour static water toxicity tests. The study was conducted in vessels each having a different concentration of the test compound, also included were water and solvent, 0.5 ml. per liter of dimethylformamide, controls. Example 4 was tested at concentrations of 1.0, 1.8, 3.2, 5.6, 10, 18, 32 and 50 ppm. The tests, including controls, were run in duplicate. Ten daphnids were introduced to each vessel. Concentrations of test compounds of 1.8 mg/l and higher resulted in a precipitate. The 48 hour effective concentration to have an effect on 50% of the daphnids was estimated to be for example 4 close to its solubility limits, i.e., between 1.0 and 3.2 mg/l.

g) Rainbow Trout and Bluegill Sunfish

The static water 96-hour acute toxicity of rainbow trout (Salmo gairdneri) and bluegill sunfish (Lepomis macrochirus) to example 4 was determined. The studies were conducted at concentrations of 0.32, 0.56, 1.0, 1.8, 3.2, 5.6 and 100 mg/l of example 4 with ten fish of each type per concentration, except the 100 mg/l concentration which was run in triplicate. Concentrations of example 4 of 1.8 mg/l and higher resulted in a precipitate. The studies also included water controls and solvent, dimethyl formamide at 0.1 mg/l, controls each with ten fish per vessel. Thirty minutes after the test compounds were added to the chambers, the fish were added by random assignment. The 96 hour LC_{50} values

for example 4 for both rainbow trout and bluegill sunfish were greater than 100 mg/l.

Example 4 was also tested against carp and exhibited low toxicity.

The insecticidal compounds used in the present invention may be used in low dosages in controlling pests. The dosage depends on a variety of factors, for example, the substance used, the kind of pest, the formulation used, the state of the crop infected with the pest and the prevailing weather conditions. In general, for the control of pests in rice, a dosage corresponding to from about 10 gm. to about 10,000 gm of the active substance per hectare may be used and from about 50 gm. to about 1,000 gm. per hectare of the active substance is preferred.

The compounds of Formula I can be utilized in the form of compositions or formulations. In these compositions and formulations, the active substance is mixed with conventional inert (i.e., plant compatible and/or pesticidally inert) diluents or extenders such as solid carrier material or liquid carrier material of the type usable in conventional compositions or formulations. If desired, adjuvants such as surfactants, stabilizers, antifoam agents and antidrift agents may also be combined. Examples of compositions and formulations are aqueous solutions and dispersions, dusting powders, granules, oily solutions, oil dispersions, pastes, wettable powders, emulsifiable concentrates, flowables, baits, invert emulsions, aerosol compositions and fumigating candles. Compositions and formulations are prepared in a known manner, for instance by extending the active compounds with conventional dispersible liquid diluent carriers and/or dispersible solid carriers optionally with the use of carrier

vehicle assistants, e.g., conventional surface-active agents, including emulsifying agents and/or dispersing agents.

The compounds used in the present invention may be employed alone or in the form of mixtures with one another and/or with such solid and/or liquid dispersible carrier vehicles and/or with other known compatible active agents, especially plant protection agents, such as other arthropodicides, nematocides, fungicides, bactericides, rodenticides, herbicides, fertilizers, growth-regulating agents, synergists, etc., if desired, or in the form of particular dosage preparations for specific applications made therefrom, such as solutions, emulsions, suspensions, powders, pastes and granules which are thus ready for use.

In the compositions of the present invention the active compound is generally present in an amount substantially between about 0.0001 percent and 99 percent by weight and preferably between about 1% and 75% by weight. Mixtures suitable for direct application or field application generally contemplate those in which the active compound is present in an amount substantially between about 0.0001 percent and 5 percent, preferably between about 0.001 percent and 3 percent, by weight of the mixture.

The present invention contemplates overall compositions which comprise mixtures of a conventional dispersible carrier such as (1) a dispersible inert, finely divided carrier solid, and/or (2) a dispersible carrier liquid such as an inert organic solvent and/or water, preferably including a surface-active effective amount of a carrier vehicle assistant, (e.g., a surface-active agent, such as an emulsifying

agent and/or a dispersing agent), and an amount of the active compound which is effective for the purpose desired.

The active compounds can be applied as sprays by methods commonly employed, such as conventional high-gallonage hydraulic sprays, low gallonage sprays, ultra-low-volume sprays, airblast sprays, aerial sprays and dusts as is known in the art. The active compounds can also be strewn mechanically or by hand as dusts or granules.

Furthermore, the present invention contemplates methods of selectively killing, combating or controlling pests, which comprise applying to at least one of (a) such pests and (b) the corresponding habitat thereof (i.e., the locus to be protected, for example, to a growing crop or to an area where a crop is to be grown) a correspondingly combative or toxic amount (i.e., a pesticidally effective amount) of the particular active compound of the invention alone or together with a carrier vehicle as noted above.

It will be realized, of course, that the concentration of the particular active compound utilized in admixture with the carrier vehicle will depend upon such factors as the type of equipment employed, method of application, area to be treated, types of pests to be controlled and degree of infestation. Therefore, in special cases, it is possible to go above or below the aforementioned concentration ranges.

In addition to the aforementioned ingredients, the preparations, according to the invention, may also contain other substances commonly used in preparations of this kind. For example, a lubricant, such as calcium stearate or magnesium stearate, may be added to a wettable powder or to a mixture to be granulated. Furthermore there

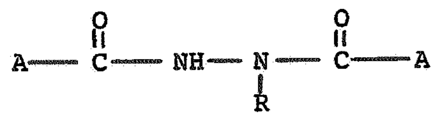
may, for example, be added "adhesives" such as polyvinylalcohol, cellulose derivatives or other colloidal materials, such as casein, to improve the adherence of the pesticide to the surface to be protected.

The compounds of the invention are also useful to control insects in seeds, generally by applying an effective amount of the compound to the surface area of the seeds to be treated. This may be accomplished by varying means common in the art, such as slurrying, soaking, dusting, spraying and the like.

Compositions and formulations according to the present invention may also include known pesticidal compounds. This expands the spectrum of activity of the preparations and may give rise to synergism.

CLAIMS

1. A method of combating insect infestation in rice, which method comprises applying an insecticidally active compound of the formula:



wherein R is <u>tert</u>-butyl or neopentyl;

A is 2-pyridyl, unsubstituted phenyl or phenyl substituted with one or two substituents each independently selected from the group consisting of 2- or 4-halo,2,3- or 2,6- dihalo, 4-(C_1-C_2)alkyl,2,3-di(C_1-C_2)alkyl, 2-(C_1-C_2)alkyl-3-halo, 2-halo-3-(C_1-C_2)alkyl 2,3-di(C_1-C_2)alkoxy and 2- or 3- (C_1-C_2)alkoxy; A' is 1-methylethenyl, unsubstituted phenyl or phenyl substituted with one or two substituents each independently selected from 2-, 3-, or 4-halo,3,5- 3,4- or 2,4-dihalo, 3-(C_1-C_2) alkyl,3,5-di(C_1-C_2)alkyl, 3-(C_1-C_2)alkyl-5-halo and 2-halo-5-(C_1-C_2)alkyl, provided A and A' are not both unsubstituted phenyl; or an agronomically-acceptable salt thereof, optionally in a composition additionally comprising an agronomically acceptable diluent or carrier; to either growing rice plants, or rice seeds, or an area where or a medium in which rice plants are to be grown or are growing.

2. The method of claim 1 wherein R is <u>tert</u>-butyl, A is 2-pyridyl, unsubstituted phenyl or phenyl substitued with one or two substituents each independently selected from the group consisting of 2- or 4-halo,2,3- or 2,6-dihalo, 4-(C_1-C_2)alkyl,2,3-di(C_1-C_2)alkyl, 2-(C_1-C_2)alkyl-3-halo, 2,3-di(C_1-C_2)alkoxy and 2-halo-3-(C_1-C_2)alkyl; A' is unsubstituted phenyl or phenyl subsituted with one or two substitutents each independently selected from 2-,3-, or 4-halo,3,5- 3,4- or 2,4-dihalo, 3-(C_1-C_2)alkyl, 3,5-di(C_1-C_2)alkyl, 3-(C_1-C_2)alkyl-5-halo and

2-halo-5-(C_1-C_2)alkyl,provided A and A' are not both unsubstituted phenyl; or an agronomically-acceptable salt thereof.

3. The method of claim 2 wherein A is unsubstituted phenyl or phenyl substituted with one or two substituents each independently selected from the group consisting of 4-halo,4-(C_1C_2)alkyl, 2,3-di(C_1-C_2)alkyl and 2,6-dihalo; and A' is phenyl substituted with one or two substituents each independently selected from the group consisting of 2-halo, 2,4-dihalo, 3-(C_1-C_2)alkyl and 3,5-di(C_1-C_2)alkyl; or an agronomically-acceptable salt thereof.

4. The method of claim 3 wherein A is phenyl substituted with 4-methyl, 4-ethyl, 2,6-difluoro or 2,3-dimethyl and A' is phenyl substituted with 2-chloro, 2,4-dichloro, 2-chloro-4-fluoro, 3-methyl or 3,5-dimethyl; or an agronomically-acceptable salt thereof.

5. The method of claim 4 wherein the compound is, 1-(3,5-dimethylbenzoyl)-2-(4-ethylbenzoyl)-1-tert-butylhydrazine, 1-(3-methylbenzoyl)-2-(2,3-dimethylbenzoyl)-1-tert-butyhydrazine, 1-(3,5-dimethylbenzoyl)-2-(4-methylbenzoyl)-1-tert-butylhydrazine, 1-(2-chloro-4-fluorobenzoyl)-2-benzoyl-1-tert-butylhydrazine or 1-(2-4-dichlorobenzoyl)-2-(2,6-difluorobenzoyl)-1-tert-butylhydrazine.

6. The method of any one of claims 1 to 5 wherein the active compound is applied to a field, in which the rice is growing or is to be grown, at a rate of 10 grams to 10,000 grams of the active compound per hectare.

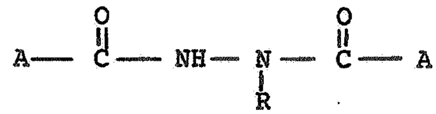
7. The method of claim 6 wherein the active compound is applied to the field at a rate of 50 grams to 1,000 grams of the active compound per hectare.

8. The method of any one of the preceding claims wherein the insects are members of the insect orders Lepidoptera and Homoptera.

9. The method of claim 8 wherein the insects are rice stem borers or rice leaffolders or green rice leafhoppers.

10. A vendible article comprising:

1. a container
2. an insecticidally active compound of the formula:



wherein R is <u>tert</u>-butyl or neopentyl;

A is 2-pyidyl, unsubstituted phenyl or phenyl substituted with one or two substituents each independently selected from the group consisting of 2- or 4-halo,2,3- or 2,6- dihalo, 4-(C_1-C_2)alkyl,2,3-di(C_1-C_2)alkyl, 2-(C_1-C_2)alkyl-3-halo, 2-halo-3-(C_1-C_2)alkyl 2,3-di(C_1-C_2)alkoxy and 2- or 3- (C_1-C_2)alkoxy; A' is 1-methylethenyl, unsubstituted phenyl or phenyl substituted with one or two substituents each independently selected from 2-, 3-, or 4-halo,3,5- 3,4- or 2,4-dihalo, 3-(C_1-C_2) alkyl,3,5-di(C_1-C_2)alkyl, 3-(C_1-C_2)alkyl-5-halo and 2-halo-5-(C_1-C_2)alkyl, provided A and A' are not both unsubstituted phenyl; or an agronomically-acceptable salt thereof, contained within the container; and (3) instructing information comprising written and/or illustrative information for applying the active compound to either growing rice plants, or rice seeds, or an area where or a medium which rice plants are to be grown or are growing.

11. The article of claim 10 wherein R is <u>tert</u>-butyl, A is 2-pyridyl, unsubstituted phenyl or phenyl substituted with one or two substituents each independently selected from the group consisting of 2- or 4-halo, 2,3- or 2,6-dihalo, 4-(C_1-C_2)alkyl, 2,3-di(C_1-C_2)alkyl, 2-(C_1-C_2)alkyl-3-halo, 2,3-di(C_1-C_2)alkoxy and 2-halo-3-(C_1-C_2)alkyl; A' is unsubstituted phenyl or phenyl substituted with one or two substituents each independently selected from 2-, 3-, or 4-halo, 3,5- 3,4- or 2,4-dihalo, 3-(C_1-C_2)alkyl, 3,5-di(C_1-C_2)alkyl, 3-(C_1-C_2)alkyl-5-halo and 2-halo-5-(C_1-C_2)alkyl, provided A and A' are not both unsubstituted phenyl; or an agronomically-acceptable salt thereof.

12. The article of claim 11 wherein A is unsubstituted phenyl or phenyl substituted with one or two substituents each independently selected from the group consisting of 4-halo, 4-(C_1-C_2)alkyl, 2,3-di(C_1-C_2)alkyl and 2,6-dihalo; and A' is phenyl substituted with one or two substitutents each independently selected from the group consisting of 2-halo, 2,4-dihalo and 3,5-di(C_1-C_2)alkyl; or an agronomically-acceptable salt thereof.

13. The article of claim 12 wherein A is phenyl substitited with 4-methyl, 4-ethyl, 2,6-difluoro or 2,3-dimethyl and A' is phenyl substituted with 2-chloro, 2,4-dichloro, 2-chloro-4-fluoro, 3-methyl or 3,5-dimethyl; or an agronomically-acceptable salt thereof.

14. The article of claim 13 wherein the compound is, 1-(3,5-dimethylbenzoyl)-2-(4-ethylbenzoyl)-1-tert-butylhydrazine, 1-(3-methylbenzoyl)-2-(2,3-dimethylbenzoyl)-1-tert-butylhyrazine, 1-(3,5-dimethylbenzoyl)-2-(4-methylbenzoyl)-1-tert-butylhydrazine, 1-(2-chlorobenzoyl)-2-(2,6-difluorobenzoyl)-1-tert-butylhydrazine or 1-(2,4-dichlorobenzoyl)-2-(2,6-difluorobenzoyl)-1-tert-butylhydrazine.

15. The article as claimed in any one of claims 10 to 14, wherein the insecticidally active compound is in a composition which, in addition to said active compound, comprises agronomically acceptable diluent or carrier.

16. An article as claimed in any one of claims 10 to 15, wherein the container is a box, pail or drum.

17. An article as claimed in any one of claims 10 to 15, wherein the container is a canister.

18. The article as claimed in any one of claims 10 to 17 wherin the instructing information is on an outside surface of the container.

19. The article as claimed in any one of claims 10 to 17 wherin the instructing information is on an inside surface of the container.

20. The article as claimed in any one of claims 10 to 17, wherein the instructing information is on a sheet of paper or other suitable substrate.

21. The article as claimed in claim 19 except when dependent on claim 17, wherein the sheet of paper or other suitable substrate is contained within the container.

22. A composition comprising an insecticidally active compound as defined in any one of claims 1-5 and an agronomically acceptable diluent or carrier wherein said composition is intended for use in combating infestation in rice.

23. An insecticidal composition for use in rice fields comprising a carrier acceptable for use on rice and an insecticidally-effective amount of a compound of the formula:

$$A - \overset{\overset{\displaystyle O}{\|}}{C} - NH - \underset{\underset{\displaystyle R}{|}}{N} - \overset{\overset{\displaystyle O}{\|}}{C} - A'$$

wherein R is <u>tert</u>-butyl or neopentyl;

A is 2-pyridyl, phenyl or phenyl substituted with one or two substituents each independently selected from the group consisting of 2- or 4-halo, 2,3- or 2,6-dihalo,4-(C_1-C_2)alkyl, 2,3-di(C_1-C_2)alkyl, 2-(C_1-C_2)alkyl-3-halo, 2-halo-3-(C_1-C_2)alkyl, 2,3-di(C_1-C_2)alkoxy and 2- or 3-(C_1-C_2)alkoxy; A' is 1-methylethenyl, phenyl or phenyl substituted with one or two substituents each independently selected from 2-,3-, or 4-halo 3,5- 3,4- or 2,4-dihalo, 3-(C_1-C_2)alkyl, 3,5-di(C_1-C_2)alkyl, 3-(C_1-C_2)alkyl-5-halo, 2-halo-5-(C_1-C_2)alkyl, provided A and A' are not both phenyl; and agronomically-acceptable salts thereof.

24. The insecticidal composition of claim 23 wherein R is <u>tert</u>-butyl, A is 2-pyridyl, phenyl or phenyl substituted with one or two subsituents each independently selected from the group consisting of 2- or 4-halo, 2,3- or 2,6-dihalo, 4-(C_1-C_2)alkyl, 2,3-di(C_1-C_2)alkyl, 2-(C_1-C_2)alkyl-3-halo, 2,3-di(C_1-C_2)alkoxy and 2-halo-3-(C_1-C_2)alkyl; A' is phenyl or phenyl substituted with one or two subsituents each independently selected from 2-,3-, or 4-halo,3,5- 3,4- or 2,4-dihalo, 3-(C_1-C_2)alkyl, 3,5-di(C_1-C_2)alkyl, 3-(C_1-C_2)alkyl-5-halo and 2-halo-5-(C_1-C_2)alkyl, provided A and A' are not both phenyl; and agronomically-acceptable salts thereof.

25. The insecticidal composition of claim 24 wherein A is phenyl or phenyl substituted with one or two subsituents each independently selected from the group consisting of 4-halo, 4-(C_1-C_2)alkyl, 2,3-di(C_1-C_2)alkyl and 2,6-dihalo; and A' is phenyl subsituted with one or two subsituents each independently selected from the group consisting of 2-halo, 2,4-dihalo and 3,5-di(C_1-C_2)alkyl; and agronomically-acceptable salts thereof.

26. The insecticidal composition of claim 25 wherein A phenyl substituted with 4-methyl, 4-ethyl, 2,6-difluoro or 2,3-dimethyl and A' is phenyl substituted with 2-chloro,2,4-dichloro, 2-chloro-4-fluoro, 3-methyl or 3,5-dimethyl; and agronomically-acceptable salts thereof.

27. The insecticidal composition of claim 26 wherein the compound is, 1-(3,5-dimethylbenzoyl)-2-(4-ethylbenzoyl)-1-*tert*-butylhydrazine, 1-(3-methylbenzoyl)-2-(2,3-dimethylbenzoyl)-1-*tert*-butylhydrazine, 1-(3,5-dimethylbenzoyl)-2-(4-methylbenzoyl)-1-*tert*-butylhydrazine, 1-(2-chloro-4-fluorobenzoyl)-2-benzoyl-1-*tert*-butylhydrazine or 1-(2,4-dichlorobenzoyl)-2-(2,6-difluorobenzoyl)-1-*tert*-butylhydrazine.

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